Nonequilibrium Work Relation in Macroscopic System

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We reconsider a well-known relationship between the fluctuation theorem and the second law of thermodynamics by evaluating a probability measure-valued process. In order to establish a bridge between microscopic and macroscopic behaviors, we consider the thermodynamic limit of a stochastic dynamical system following the fundamental procedure often used in statistical mechanics. The thermodynamic path characterizing a macroscopic dynamical behavior can be formulated as an infimum of the action functional for the probability measure-valued process. In our formulation, the second law of thermodynamics can be derived by symmetry of the action functional, which is generated from the fluctuation theorem. We find that our formulation not only confirms that the ordinary Jarzynski equality in the thermodynamic limit can be rederived, but also enables us to establish a nontrivial nonequilibrium work relation for metastable states.

Introduction– The Jarzynski equality $\left\langle e^{-\beta W}\right\rangle_{\rm eq} = e^{-\beta\Delta\Phi_{\rm eq}}$, where $\Delta\Phi_{\rm eq}$ is a free-energy difference, plays a role as a bridge between the symmetry of microscopic dynamics, the fluctuation theorem, and the fundamental limitation on time evolution of macroscopic quantities, the second law of thermodynamics [1–4]. We usually term the Jarzynski equality as generalization of the second law of thermodynamics from the fact that Jensen's inequality for the Jarzynski equality yields its form as $\langle W\rangle_{\rm eq} \geq \Delta\Phi_{\rm eq}$. The present study does not aim at giving any objection against the validity of the Jarzynski equality. However, we would like to ask the following fundamental question on the above ordinary understanding on the relationship between the Jarzynski equality and the second law of thermodynamics. Does $\langle W\rangle_{\rm eq}$ express the performed work in thermodynamics?

The reasons for this question are as follows. Let us go back to a starting point of statistical physics and its connection with thermodynamics. To elucidate macroscopic properties from a microscopic description of the system, we consider an infinite-number limit of the sample mean, which is a coarse-grained picture of the system. On the other hand, the performed work given in the Jarzynski equality $\langle W\rangle_{\rm eq}$ has not been baptized yet through this ordinary procedure. In terms of statistical mechanics, expectations coincide a global minimum of the rate function, which describes the observed value in the thermodynamic limit. More precisely, the performed work written in the ordinary Jarzynski equality is not yet expressed by the global minimum of the rate function. In addition, the rate function can possess not only the global minimum but also several local minima, which represents the existence of so-called metastable states. Such a system does not always relax to equilibrium state within a time scale in a practical experience. From the above considerations, we cannot readily regard the performed work $\langle W\rangle_{\rm eq}$ in the Jarzynski equality as that in the macroscopic system. This problem motivates us to compute the performed work in the thermodynamic limit by directly evaluating the dynamics for the coarse-grained quantity, which can be described by a probability measure-valued process [5].

We analyze the probability measure-valued process in the following strategy. At first, we evaluate the entropy production of the system from the action functional [6, 7], the rate function for the probability measure-valued process, which describes contributions around the representative path of the time evolution in the thermodynamic limit. The second law of thermodynamics can be rederived from the symmetry of this action functional, which is generated from the fluctuation theorem. This formulation is written in terms of the rate function, which is different from the ordinary derivation through the Jarzynski equality as introduced above. This is one of our main results in the present study. These analyses provide deep understanding on the connection between the fluctuation theorem and the second law of thermodynamics and bring us another nontrivial result. Owing to the analysis aiming at the thermodynamic limit, the symmetry of the action functional can reveal the form of the rate function for metastable states. This form enables us to establish a nontrivial nonequilibrium work relation for metastable states. The resulting work relation can be expressed in the same useful form as the Jarzynski equality in the limited cases with appropriate protocols related with relaxation processes toward the selected metastable state.

$$\left\langle e^{-N\beta w}\right\rangle_i = e^{-N\beta\{\phi_{\rm eq}(\beta,\lambda_T)-\phi_i(\beta,\lambda_0)\}}, \tag{1}$$

where N is the number of components in the system we deal with, w is the performed work per component, and $\phi_{\rm eq}$ is the free energy per component for the last equilibrium state while ϕ_i is that for the initial metastable state

distinguished by an index i. By use of our nonequilibrium work relation, we can compute the free energy for the metastable state due to the same form as the Jarzynski equality. The existence of the metastable state is considered to be related with peculiar relaxation dynamics as in the glassy systems. Our result would provide a significant insight for understanding the special behavior observed in such complicated systems. In the remains of the paper, we describe our analysis in detail.

Action functional for mean-field dynamics– Let us consider that the system consists of N components $\{x_i\}\,(i=1\cdots N)$ and is attached to heat bath with an inverse temperature β. The work is performed into the system by controlling external parameter λ. Let us make two additional assumptions for the system in our study. First, the dynamics is described by Ito stochastic process, which satisfies the fluctuation theorem, as

$$dx_i = \left[-\frac{\partial}{\partial x_i}H_N\left(\{x_i\},\lambda_t\right)\right]dt + \sqrt{\frac{2}{\beta}}d\xi_i, \qquad (2)$$

where ξ_i denotes the Wiener process, and $H\left(\{x_i\},\lambda\right)$ is the Hamiltonian of the system [3, 4, 8]. Second, the Hamiltonian is represented as two-body interactions with all the components (i.e. mean field),

$$H_N\left(\{x_i\},\lambda\right) = -\sum_i F_\lambda\left(x_i\right) - \frac{1}{2N}\sum_{ij} G\left(x_i, x_j\right), \quad (3)$$

where F_λ stands for the potential trap, G is the two-body interaction and symmetric $G\left(x,y\right) = G\left(y,x\right)$. In this dynamical system, we analyze probability measure-valued process, which is the time evolution of the empirical measure as $\mu\left(x,t\right) = (1/N)\,\Sigma_i\delta\left(x_i - x\right)$ [5, 6, 9, 10]. It is straightforward to obtain

$$\delta\mu\left(x,t\right) = D_{\mu_t,\lambda_t}\left(x\right)dt + \frac{1}{N}\sqrt{\frac{2}{\beta}}\sum_i\frac{\partial\delta\left(x_i - x\right)}{\partial x_i}d\xi_i, \quad (4)$$

where

$$\begin{aligned} D_{\mu_t,\lambda_t}\left(x\right) &= -\frac{\partial}{\partial x}\left\{f_{\lambda_t}\left(x\right)\mu\left(x,t\right)\right\} \\ &-\frac{\partial}{\partial x}\left\{\mu\left(x,t\right)\int g\left(x,y\right)\mu\left(y,t\right)dy\right\} + \frac{1}{\beta}\frac{\partial^2\mu\left(x,t\right)}{\partial x^2}. \end{aligned} \qquad (5)$$

Here we use $f_{\lambda_t}\left(x\right) = \partial F_{\lambda_t}\left(x\right)/\partial x$ and $g\left(x,y\right) = \partial G\left(x,y\right)/\partial x$. From Eq. (4), we derive the functional Fokker-Planck equation as

$$\begin{aligned} \frac{\partial}{\partial t}Prob_t\left[\mu\right] &= \int dx\frac{\delta}{\delta\mu\left(x\right)}\left\{-D_{\mu,\lambda_t}\left(x\right)Prob_t\left[\mu\right]\right\} \\ &+\frac{1}{2N}\iint dxdy\frac{\delta^2}{\delta\mu\left(x\right)\delta\mu\left(y\right)}\left\{R_\mu\left(x,y\right)Prob_t\left[\mu\right]\right\}, \end{aligned} \qquad (6)$$

where $Prob_t[\mu]$ is the probability for the empirical measure and $R_\mu\left(x,y\right)$ denotes a metric of the probability measure-valued process as

$$R_\mu\left(x,y\right) = \frac{2}{\beta}\int dz\frac{\partial\delta\left(x-z\right)}{\partial z}\frac{\partial\delta\left(y-z\right)}{\partial z}\mu\left(z\right). \qquad (7)$$

In order to elucidate the macroscopic behavior of the system, let us consider the thermodynamic limit ($N\to\infty$) on Eq. (4). We reach a nonlinear diffusion equation for the empirical measure $\mu(x,t)$, which represents thermodynamic time evolution of the system,

$$\frac{\partial\mu\left(x,t\right)}{\partial t} = D_{\mu_t,\lambda_t}\left(x\right). \qquad (8)$$

Next, in order to examine the fluctuation from the solution of Eq. (8) in a sufficient large N, we analyze the conditional path probability for the stochastic dynamics govened by the functional Fokker-Planck equation Eq. (6). We denote the conditional path probability during the time interval $[0,T]$ as $Path\left[\lambda,\mu|\mu_0\right] = e^{-NJ_{[0,T]}[\lambda,\mu]}$. Here, $J_{[0,T]}\left[\lambda,\mu\right]$ is called the action functional given as,

$$J_{[0,T]}\left[\lambda,\mu\right] = \int_0^T dtL_{\lambda_t}\left[\dot{\mu_t},\mu_t\right]. \qquad (9)$$

The Lagrangian $L_{\lambda_t}\left[\dot{\mu_t},\mu_t\right]$ is obtained by using Eq. (6) as [7, 11, 12]

$$\begin{aligned} L_{\lambda_t}\left[\dot{\mu_t},\mu_t\right] &= \frac{1}{2}\iint R^{-1}_{\mu_t}\left(x,y\right)\left\{\dot{\mu}\left(x,t\right) - D_{\mu_t,\lambda_t}\left(x\right)\right\} \\ &\times\left\{\dot{\mu}\left(y,t\right) - D_{\mu_t,\lambda_t}\left(y\right)\right\}dxdy. \end{aligned} \qquad (10)$$

We find a useful identity from the property on the inverse metric $R^{-1}_{\mu_t}$ as $\int d\alpha R_{\mu_t}\left(x,\alpha\right)R^{-1}_{\mu_t}\left(\alpha,y\right) = \delta\left(x-y\right)$,

$$-\frac{\partial}{\partial x}\left\{\mu\left(x,t\right)\frac{\partial R^{-1}_{\mu_t}\left(x,y\right)}{\partial x}\right\} = \frac{\beta}{2}\delta\left(x-y\right). \qquad (11)$$

By use of this identity, we can reveal the symmetry of the action functional according to the fluctuation theorem given by the ratio of the time forward path probability written by $L_{\lambda_t}\left[\dot{\mu_t},\mu_t\right]$ and the time backward one by $L_{\hat{\lambda}_{\hat{t}}}\left[\dot{\hat{\mu}}_{\hat{t}},\hat{\mu}_{\hat{t}}\right]$, where $\hat{\mu}_{\hat{t}} = \mu_t,\ \hat{t} = T-t$. The ratio indeed gives

$$\begin{aligned} L_{\lambda_t}\left[\dot{\mu_t},\mu_t\right] &= L_{\hat{\lambda}_{\hat{t}}}\left[\dot{\hat{\mu}}_{\hat{t}},\hat{\mu}_{\hat{t}}\right] \\ &-2\iint dxdyR^{-1}_{\mu_t}\left(x,y\right)D_{\mu_t,\lambda_t}\left(x\right)\dot{\mu_t}\left(y\right). \end{aligned} \qquad (12)$$

By using the identity Eq. (11), the second term in Eq. (12) is evaluated as $\int dx\left\{\delta I_{\mathrm{eq},\lambda_t}\left[\mu_t\right]/\delta\mu_t\left(x\right)\right\}\dot{\mu_t}\left(x\right)$. Here, we employ the rate function $I_{\mathrm{eq},\lambda}\left[\mu\right]$ for the canonical distribution $\exp(-\beta H_N)/Z_N$ with the external parameter λ, where Z_N is the partition function. This rate

function is given as $I_{\mathrm{eq},\lambda}[\mu]=\beta\epsilon_\lambda[\mu]-s[\mu]-\beta\phi_{\mathrm{eq}}(\beta,\lambda)$, where ϵ_λ, s and ϕ_{eq} represent the energy per component, the same form as the Shannon entropy and the free energy per component, respectively [12]. By substituting Eq. (12) into Eq. (9), we find that the symmetry of action functional $J_{[0,T]}[\lambda,\mu]$ can be written as

$$\begin{aligned}&I_{\mathrm{eq},\lambda_0}[\mu_0]+J_{[0,T]}[\lambda,\mu]+\beta w_{[0,T]}[\lambda,\mu]\\&=I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0]+J_{[0,T]}\left[\hat{\lambda},\hat{\mu}\right]\\&+\beta\left\{\phi_{\mathrm{eq}}(\beta,\lambda_T)-\phi_{\mathrm{eq}}(\beta,\lambda_0)\right\},\end{aligned}\tag{13}$$

where $w_{[0,T]}$ denotes the actual work per component performed by the external protocol λ during the time interval $[0,T]$ as $w_{[0,T]}[\lambda,\mu]=\displaystyle\int_0^T dt\dot{\lambda}_t\partial\epsilon_{\lambda_t}[\mu_t]/\partial\lambda_t$. This symmetry stands for the fluctuation theorem described by the action functional and allows us to formulate the second law of thermodynamics in terms of the work as usually used in thermodynamics.

The second law of thermodynamics– Now we are in the position to end the discussion on the second law of thermodynamics starting from the coarse-grained picture of the system. In terms of the action functional, the thermodynamic path μ^*, which denotes a solution of Eq. (8), must satisfy $J_{[0,T]}[\lambda,\mu^*]=\inf_\mu J_{[0,T]}[\lambda,\mu]$, i.e. $J_{[0,T]}[\lambda,\mu^*]=0$. Since the second law of thermodynamics is written in the inequality form, which connects the performed work and the free-energy difference between two different equilibrium states, we choose the initial condition of Eq. (8) as the equilibrium state $\mu_{\mathrm{eq},\lambda_0}$, which holds $I_{\mathrm{eq},\lambda_0}[\mu_{\mathrm{eq},\lambda_0}]=0$. Thus, the thermodynamic path $\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]$ launched from the equilibrium state satisfies

$$I_{\mathrm{eq},\lambda_0}[\mu_{\mathrm{eq},\lambda_0}]+J_{[0,T]}[\lambda,\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]=0.\tag{14}$$

Substituting Eq. (14) into Eq. (13), we obtain

$$\begin{aligned}&\beta w_{[0,T]}[\lambda,\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]\\&=I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]+J_{[0,T]}\left[\hat{\lambda},\hat{\mu}^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]\right]\\&+\beta\left\{\phi_{\mathrm{eq}}(\beta,\lambda_T)-\phi_{\mathrm{eq}}(\beta,\lambda_0)\right\},\end{aligned}\tag{15}$$

where $\hat{\mu}^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]$ denotes the time-reversal thermodynamic path $\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]$, $\hat{\mu}_0^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]$ is its initial condition and $w[\lambda,\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]$ stands for the work performed on the system which is termed in thermodynamics.

Since $I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]+J_{[0,T]}\left[\hat{\lambda},\hat{\mu}^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]\right]\geq 0$, we find the second law of thermodynamics $w_{[0,T]}[\lambda,\mu^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]\geq\phi_{\mathrm{eq}}(\beta,\lambda_T)-\phi_{\mathrm{eq}}(\beta,\lambda_0)$. In addition, the entropy production $\sigma[\lambda]$ can be written as

$$\sigma[\lambda]=\frac{1}{\beta}\left(I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]]+J_{[0,T]}\left[\hat{\lambda},\hat{\mu}^*[\lambda;\mu_{\mathrm{eq},\lambda_0}]\right]\right).\tag{16}$$

This relation implies the fluctuation dissipation relation since the action functional describes the fluctuation around the thermodynamic path. Notice that, in our formulation, the second law of thermodynamics is derived without recourse to the Jarzynski equality.

Before closing this section, we show the derivation of the ordinary Jarzynski equality from Eq. (13). Suppose that the system is set in an initial equilibrium state. We can evaluate the expectation of the exponentiated work by employing Varadhan's theorem [12, 13] and obtain

$$\left\langle e^{-N\beta w}\right\rangle_{\mathrm{eq}}=e^{-N\inf_\mu\left(I_{\mathrm{eq},\lambda_0}[\mu_0]+J_{[0,T]}[\lambda,\mu]+\beta w_{[0,T]}[\lambda,\mu]\right)}.\tag{17}$$

Here, using Eq. (13), we obtain the Jarzynski equality

$$\begin{aligned}\left\langle e^{-N\beta w}\right\rangle_{\mathrm{eq}}&=e^{-N\beta\Delta\phi_{\mathrm{eq}}}\times e^{-N\inf_{\hat{\mu}}\left(I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0]+J_{[0,T]}[\hat{\lambda},\hat{\mu}]\right)}\\&=e^{-N\beta\Delta\phi_{\mathrm{eq}}},\end{aligned}\tag{18}$$

where $\Delta\phi_{\mathrm{eq}}=\phi_{\mathrm{eq}}(\beta,\lambda_T)-\phi_{\mathrm{eq}}(\beta,\lambda_0)$ and we use $\inf_{\hat{\mu}}\left(I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0]+J_{[0,T]}\left[\hat{\lambda},\hat{\mu}\right]\right)=0$.

Nonequilibrium work relation for metastable states– We give remarks on several properties of metastable states. First, we show how metastable states emerge in relaxation process. Suppose that the system is not perturbed during relaxation process. We choose the external parameter λ as constant c. The thermodynamic time evolution is given by the nonlinear diffusion equation Eq. (8). Thus, metastable states and equilibrium state are given as fixed points of this equation. In order to obtain the fixed points of Eq. (8), we examine the Lyapunov function. We find that the rate function $I_{\mathrm{eq},c}[\mu]$ plays a roll of the Lyapunov function as

$$\begin{aligned}\frac{dI_{\mathrm{eq},c}[\mu]}{dt}&=-\beta\int dx\mu(x,t)\\&\times\left\{f_c(x)+\int g(x,y)\mu(y,t)\,dy-\frac{1}{\beta}\frac{\partial\log\mu(x,t)}{\partial x}\right\}^2\\&\leq 0.\end{aligned}\tag{19}$$

Thus the metastable states and equilibrium state are given as local minima and a global minimum of $I_{\mathrm{eq},c}[\mu]$, respectively [see Fig.1]. Second, let us show the rate function for metastable states. Suppose that the system has n metastable states. We then focus ith metastable state denoted by $\mu_{i,c}$. The rate function for this metastable state can be represented as [6, 7, 12]

$$V_{i,c}[\nu]=\inf_{\mu:\mu_0=\mu_{i,c},\mu_\infty=\nu}J^c_{[0,\infty]}[\mu],\tag{20}$$

where $\inf_{\mu:\mu_0=\mu_{i,c},\mu_\infty=\nu}$ represents an infimum among all the paths μ launched from $\mu_{i,c}$ to ν during the time interval $[0,\infty]$. To evaluate Eq. (20), we employ the constant protocol version of Eq, (13),

$$I_{\mathrm{eq},c}[\mu_0]+J^c_{[0,T]}[\mu]=I_{\mathrm{eq},c}[\hat{\mu}_0]+J^c_{[0,T]}[\hat{\mu}].$$

Then, we obtain the rate function for the metastable state as [6, 11] [see also Fig.1],

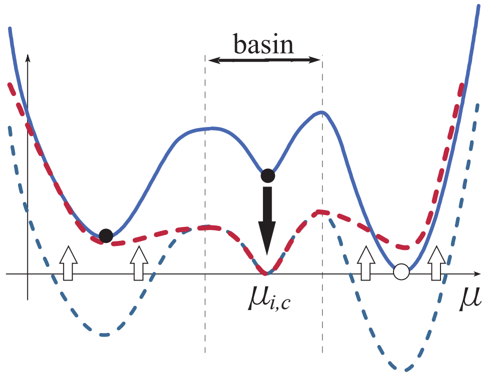

FIG. 1: (Color online) The blue curve represents the rate function for equilibrium state, $I_{\mathrm{eq},c}$. The red dashed curve denotes the rate function for ith metastable state, $V_{i,c}$. The black circles represent the metastable states, while the white circle denote the equilibrium state. The black arrow represents the downward parallel translation by $I_{\mathrm{eq},c}[\mu_{i,c}]$ of the rate function $I_{\mathrm{eq},c}$ as the blue dashed curve. The white arrows describe the modification by $A_{i,c}$ of the blue dashed curve into the red dashed curve $V_{i,c}$.

$$\begin{aligned} V_{i,c}[\nu] &= \inf_{\mu:\mu_0=\mu_{i,c},\mu_\infty=\nu} J^c_{[0,\infty]}[\mu] \\ &= \inf_{\mu:\hat{\mu}_0=\nu,\hat{\mu}_\infty=\mu_{i,c}} \Big(I_{\mathrm{eq},c}[\hat{\mu}_0] + J^c_{[0,\infty]}[\hat{\mu}] - I_{\mathrm{eq},c}[\hat{\mu}_\infty] \Big) \\ &= I_{\mathrm{eq},c}[\nu] - I_{\mathrm{eq},c}[\mu_{i,c}] + A_{i,c}[\nu], \end{aligned} \tag{21}$$

where $A_{i,c}[\nu]$ denotes a functional,

$$A_{i,c}[\nu] = \begin{cases} 0 & \text{if } \nu \text{ in basin of } \mu_{i,c} \\ \text{positive} & \text{others} \end{cases}. \tag{22}$$

Notice that we do not need to reveal the explicit form of $A_{i,c}[\nu]$ to obtain the final result.

Let us give a nontrivial nonequilibrium work relation for metastable states by use of the above functionals. Suppose that the system is initially set in ith metastable state, which differs from the initial condition of the ordinary Jarzynski equality. The expectation of the exponentiated work is then evaluated as, by using the same procedure as the above case for the Jarzynski equality,

$$\left\langle e^{-N\beta w} \right\rangle_i = e^{-N\inf_\mu \left(V_{i,\lambda_0}[\mu_0] + J_{[0,T]}[\lambda,\mu] + \beta w_{[0,T]}[\lambda,\mu] \right)}. \tag{23}$$

By Eqs. (13) and (21), we reach

$$\begin{aligned} \left\langle e^{-N\beta w} \right\rangle_i &= e^{-N\beta\{\phi_{\mathrm{eq}}(\beta,\lambda_T) - \phi_i(\beta,\lambda_0)\}} \\ &\times e^{-N\inf_{\hat{\mu}} \left(I_{eq,\hat{\lambda}_0}[\hat{\mu}_0] + J_{[0,T]}\left[\hat{\lambda},\hat{\mu}\right] + A_{i,\hat{\lambda}_T}[\hat{\mu}_T] \right)}, \end{aligned} \tag{24}$$

where we use free energy per component of ith metastable state, $\phi_i(\beta,\lambda) = (1/\beta)\, I_{\mathrm{eq},\lambda}\left[\mu^*_{i,\lambda}\right] + \phi_{\mathrm{eq}}(\beta,\lambda)$ [6, 12]. Notice that the infimum in Eq. (24), $\inf_{\hat{\mu}} \left(I_{\mathrm{eq},\hat{\lambda}_0}[\hat{\mu}_0] + J_{[0,T]}\left[\hat{\lambda},\hat{\mu}\right] + A_{i,\hat{\lambda}_T}[\hat{\mu}_T] \right)$, cannot be always equal to zero for any λ in contrast with the case of the ordinary Jarzynski equality. Taking into account the form of the functional $A_{i,c}[\nu]$ as in Eq. (22), we find that the infimum can vanish without any additional information of the functional $A_{i,c}[\nu]$ when the time-reversal external protocol $\hat{\lambda}$ expresses the protocol toward ith metastable state from the equilibrium state. Therefore we can obtain the nonequilibrium work relation for metastable states in the same form as the Jarzynski equality, which is Eq. (1).

For the future study, we remark its realization in the actual experience in short. Suppose that we prepare a specific metastable state we are interested in by controlling the protocol λ from the initial equilibrium state. We use its inverse protocol in the actual experience. The system is driven from the selected metastable state by the inverse protocol. We compute the free energy for the metastable state by observation of the exponentiated work following Eq. (1). The detailed observation of violation of the equality by change from the inverse protocol would be significant, since the effect by choosing a different λ comes from the remaining part of Eq. (24).

Conclusion– We have provided deep understanding on the connection between the fluctuation theorem and the second law of thermodynamics, by rederiving the latter from the symmetry of the action functional. In addition, we have derived the nonequilibrium work relation for metastable states. As a result, this work relation can be expressed in the same form as the Jarzynski equality by limiting on the external protocol appropriately and enables us to compute the free energy for metastable states from the performed work.

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